United Nations Environment Programme

Distr.
LIMITED

UNEP/WG.7/14
25 February 1977

Original: ENGLISH

UNEP Meeting of Experts,
designated by governments, intergovernmental
and non-governmental organizations,
on the Ozone Layer

Washington, D.C., 1 - 9 March 1977

THE EFFECT OF CHLOROFLUOROCARBONS ON THE CONCENTRATION OF ATMOSPHERIC OZONE

submitted by

THE INTERNATIONAL CHAMBER OF COMMERCE

on behalf of

MANUFACTURING CHEMISTS ASSOCIATION

Review of Industry-Sponsored Research

THE EFFECT OF CHLOROFLUOROCARBONS ON THE CONCENTRATION OF ATMOSPHERIC OZONE

Prepared by: J. R. Soulen

December 31, 1976

This review covers the research program funded by the six U. S. and 14 foreign manufacturers of chlorofluorocarbons that is administered by the Manufacturing Chemists Association and the research undertaken internally by several of the companies.

Although there has been little new scientific information that would change the conclusions of the National Academy of Sciences reports[1,2] which were issued in September, there is continued high interest in the chlorofluorocarbon-ozone issue on the part of government agencies, industry, and certain public interest groups. It is therefore worthwhile to review the present gaps in our scientific knowledge, and the steps that are being taken to reduce them in industry-sponsored research programs. This is best done using the framework of the NAS Panel report.[1] It will be recalled that the prediction of 2-20% steady state ozone depletion, which would not be achieved for ca. 100 years, was calculated from known data and particular assumptions for (1) release rates of FC-11 and FC-12, (2) atmospheric transport of these molecules, and (3) stratospheric chemistry. The existence of as-yet-unknown factors that could substantially alter this ozone depletion estimate was clearly recognized by the NAS Panel. Indeed, their first recommendation

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1. "Halocarbons: Effects on Stratospheric Ozone," Panel on Atmospheric Chemistry, National Academy of Sciences, September 13, 1976.

2. "Halocarbons: Environmental Effects of Chlorofluoromethane Release," Committee on Impacts of Stratospheric Change, National Academy of Sciences, September 13, 1976.

for future work reads:

> "In general terms, the greatest need is for verification of stratospheric ozone chemistry thru measurements of trace atmospheric constituents, both stable and reactive. The dearth of such measurements is a serious limitation to establishing the reliability of calculations and predictions of stratospheric effects."[3]

Dr. Tukey, in his statement before the Subcommittee on the Upper Atmosphere of the U. S. Senate December 15, reemphasized the two kinds of uncertainties in the NAS reports: (1) uncertainties associated with imprecise knowledge of numerical data, which necessitated giving the predicted ozone depletion as a range of possible values from 2-20%, and (2) presently unknown factors that could drastically alter the predicted depletion, possibly taking it below the 2-20% range. As stated in the NAS Committee report, "This range does not allow for possible inadequacies in the bases of the calculation," including "essential chemical reactions not so far recognized as such" and "the possibility of unexpected effects of tropospheric sinks."[4]

Stratospheric chemistry related to the chlorofluorocarbon-ozone question was felt to be particularly uncertain by the NAS Panel. Earlier this year the molecule $ClONO_2$, which was dismissed in the earliest considerations of the fluorocarbon-ozone question, was again brought up. The NAS Panel determined that inclusion of $ClONO_2$ chemistry would reduce ozone depletion estimates by a factor of 1.85. $ClONO_2$ is just one example of how new chemistry could affect the calculated amount of ozone depletion strongly. As stated in the NAS Committee report, "The probable importance of $ClONO_2$ was a surprise. Whether or not there is another such surprise in store remains to be seen."[5]

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3. Reference 1, page F-1a.

4. Reference 2, pages 1-3,4.

5. Reference 2, page 5-12.

The NAS Panel listed six specific objectives to reduce the uncertainty in ozone depletion estimates due both to factors already known and to the possibility of finding subsequently an important unidentified factor. The most important studies, expected to require one to two years, are as follows:

1. "Establish the role of $ClONO_2$ in the stratosphere--This might be accomplished by comparing infrared measurements of its concentration with calculated results. However, particularly if disparities are revealed by such comparisons, there will need to be further study of the stratospheric processes that might convert the $ClONO_2$ back into catalytically active species."[6]

The chlorofluorocarbon industry is supporting the work of Dr. D. G. Murcray of the University of Denver in his efforts to determine the stratospheric concentration of $ClONO_2$. This support is for balloon flights to make measurements by infrared absorption spectroscopy, laboratory studies to obtain the necessary calibration spectra for $ClONO_2$, and assistance in the preparative work to obtain samples for the laboratory studies. Several more months will be required before definitive information will be available from flights carried out in 1976. On the basis of indications to date, significant amounts of $ClONO_2$ in the stratosphere are neither proved nor ruled out.

A major problem in positive identification of molecules using the infrared technique and in determining their concentration is possible interferences from other molecules that absorb in the same spectral region. Greater resolution can minimize this problem and the chlorofluorocarbon manufacturers are supporting Dr. H. J. Buijs of Bomem, Inc., to construct a new spectrometer with an anticipated resolution of 0.01 cm^{-1}. This instrument will be useful in the wavelength region of interest for $ClONO_2$ and should be completed in early 1977.

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6. Reference 1, page F-2.

For long term monitoring of stratospheric molecules, continuous ground-based observations will be much more economical than in situ measurements from balloons, airplanes, or rockets. Scientists from the Du Pont Company and the National Bureau of Standards have collaborated to determine the microwave spectrum of $ClONO_2$[7], which will be useful for both air and ground based measurements by millimeter wavelength techniques.

The rates of formation and destruction of $ClONO_2$ are important to the understanding of its stratospheric chemistry, as is knowledge of its mechanism of decomposition (e.g., photolysis, reaction) and the products of its decomposition. The chlorofluorocarbon industry is sponsoring research at the University of Illinois under Dr. J. W. Birks, who determined the rate of formation of $ClONO_2$ via the reaction $ClO + NO_2 + M \rightarrow ClONO_2 + M$ (where M is a molecule such as N_2 or He). Dr. Birks is also studying the rate of destruction of $ClONO_2$ by both homogeneous and heterogeneous reactions that could result in removal of reactive species from the catalytic ozone destruction cycle.

The photochemistry of $ClONO_2$ that is relevant to its stratospheric behavior can also be studied in the laboratory. The chlorofluorocarbon manufacturers are supporting work by Dr. J. Wiesenfeld at Cornell University and Dr. R. B. Timmons of Catholic University to determine photoabsorption characteristics and photodecomposition products of $ClONO_2$ as a function of wavelength and temperature.

2. "Verify the reliability of predicted ozone reductions--By this we mean a more direct means than has been available so far for estimating and narrowing the total uncertainty of the ozone reductions predicted for the CFMs, including the possibility of as yet unidentified processes. Observations of ClO and Cl profiles in the stratosphere and their comparison with calculated values seem to be the most likely means of accomplishing this objective. However, the analysis of any disparities probably will be difficult, and requires comparisons with simultaneous measurements of other species such as HCl and O_3. Preferably,

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7. R. D. Suenram, D. R. Johnson, L. C. Glasgow, and P. Z. Meakin, Geophys. Res. Lett. 3, 611-4, October, 1976.

the observations of ClO and Cl should be by two independent methods, such as resonance fluorescence and microwave emission in the case of ClO."[8]

An approach to verify predicted ozone reductions not emphasized in the shorter-term objectives of the NAS Panel is that based on direct observations of stratospheric ozone itself. Dr. William J. Hill and his colleagues at Allied Chemical Corporation have applied the technique of time series analysis to data from nine long-term ozone stations well-spaced around the world. Their conclusions[9] are of considerable importance:

1. No detectable abnormal decline in ozone has occurred during the six-year period 1970-75.

2. The predicted cumulative ozone depletions due to FC-11 and FC-12, subsonic and supersonic aircraft, bromine compounds, nitrogenous fertilizers, and a number of halocarbons, when treated cumulatively appear to be too large.

3. The calculated upper limit of 20% steady state depletion (ca. 100 years hence) due to FC-11 and FC-12 appears very unlikely.

4. The time series analysis of data from nine globally representative stations could detect a 1.5% abnormal ozone change. Appropriate action following this early warning could limit the maximum reversible change to only 2.3%. Use of data from a larger number of ground based or satellite stations could increase the detectability and decrease the impact on the ozone layer.

The chlorofluorocarbon manufacturers are supporting Drs. E. Parzen and M. Pagano of the State University of New York at Buffalo to carry out further research on time series analysis of ozone data. Work of this type clearly can have great importance to both the stratospheric ozone problem and the research and measurement programs addressing it by:

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8. Reference 1, page F-2.

9. W. J. Hill, P. N. Sheldon, J. J. Tiede, "Analyzing Worldwide Total Ozone for Trends," paper accepted for publication in Geophys. Res. Lett.

1. Providing a direct test of ozone depletion estimates from model calculations.

2. Maximizing the value and usefulness of the extensive ozone measurements, past, present, and future.

3. Providing a global early warning system for abnormal ozone changes, i.e., man-made or natural trends that are different from past variations.

4. Allowing practical limits to be set on the scope of the biological and climatic effects research programs in accordance with the maximum ozone change allowed by the early warning system plus appropriate action to limit the change.

To date the principal method used to test the ozone depletion theory has been indirect: measure the concentrations of certain species the amounts of which are quite small and compare the measurements with theoretical predictions. This has required the development of new data, techniques, and instruments, and the chlorofluorocarbon manufacturers have since 1974 had this as an important part of their research program. Among a number of projects relating to the analysis of ClO and other chlorine-containing species, one under the direction of Dr. D. H. Stedman at the University of Michigan measured successfully both ClO and Cl by titration with NO and detection of Cl by resonance fluorescence.[10] NASA provided support for Dr. J. G. Anderson to develop a flight instrument based on this technique and make measurements of ClO and Cl this year. The values from the several sets of measurements vary several-fold from each other, and all are higher than theory. It will therefore be important to follow up this work in accordance with the NAS recommendations for:

1. Measurement of a greater number of different species simultaneously to provide a more rigorous test of the theory and

2. Measurement of the most important species simultaneously by two different techniques to check on the accuracy of the analytical methods.

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10. D. H. Stedman, Res./Dev. 27, 22-4, 26, January, 1976.

Work supported by the chlorofluorocarbon manufacturers to help accomplish these tasks includes laboratory investigations of ultraviolet spectra of ClO by Dr. R. W. Nicholls of York University[11] and Dr. D. D. Davis of Georgia Tech and of the laser magnetic resonance technique for detection of ClO by Dr. C. J. Howard at the NOAA Laboratory at Boulder. Support is being provided for stratospheric measurements of ClO by Dr. D. G. Murcray using a balloon-borne ultraviolet spectrophotometer and to Dr. P. M. Solomon of SUNY Stony Brook for ground-based microwave measurements. In the latter program the 3 mm maser detector that will be employed will be the most sensitive receiver in the world for this type of observation.

To help resolve the serious questions that have been raised by the finding of larger than predicted amounts of chlorine species in the stratosphere, the chlorofluorocarbon manufacturers are supporting a project under Dr. A. E. J. Eggleton at AERE Harwell to develop methods for determining total chlorine and total fluorine. They are to be employed during balloon flights to compare their sum with the total amounts of these elements found with the sum of individual Cl- and F-containing molecules measured by other investigators.

3. "Develop an accurate materials balance--Inasmuch as a materials balance can detect, in principle, otherwise unidentified sinks for the CFMs, a detailed analysis should be made of how best to obtain a materials balance accurate enough to be meaningful. The study should define a minimum set of observations (including its time span) sufficient to establish a true global burden, and develop standards of sensitivity, calibration and accuracy necessary for the results to be useful. If such a study supports its feasibility, there should then be a coordinated observational program and data analysis for both F-11 and F-12."[12]

In spite of assertions to the contrary from elsewhere in the scientific community, the possibility of an unidentified sink

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11. M. Mandelman and R. W. Nicholls, "The Absorption Cross-Sections and f-Values for the v"=0 Progression of Bands and Associated Continuum for the ClO($A^2\Pi_i$-$X^2\Pi_i$) System," accepted for publication in J. Quant. Spectros. Radiat. Transfer.

12. Reference 1, pages F-2,3.

for the chlorofluorocarbons indicated above by the NAS Panel has been underscored by the NAS Committee:

> "Although the materials balance can be interpreted as consistent with little or no active removal of the CFMs, the uncertainty limits range from zero inactive removal to a rate sixfold faster than that of the stratospheric photolysis."[13]

Modeling work sponsored by the chlorofluorocarbon manufacturers led to the realization that chlorofluorocarbon measurements to date did not rule out the possibility of sinks for these molecules.[14] The most recent work indicates the most probable tropospheric lifetime for FC-11 is between 15-20 years.[15] The ozone depletion calculations in the NAS reports are based on an infinite tropospheric lifetime and would be reduced as much as five-fold by this shorter tropospheric lifetime.

In its recommendation above the NAS Panel calls for development of both strategy and techniques to determine if the materials balance approach can be successful. The chlorofluorocarbon manufacturers have encouraged one of their modeling contractors to examine measurement problems and strategy. Several reports were prepared including one that was presented to the NASA Stratospheric Research Advisory Committee in December 1975 and has appeared subsequently as a publication.[16]

Three contractors in the industry program are now studying problems of calibration and accuracy of chlorofluorocarbon

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13. Reference 2, page 5-10.

14. N. D. Sze and M. F. Wu, "Measurements of Fluorocarbons 11 and 12 and Model Validation: An Assessment," 27 pp., 15 December 1975.

15. J. P. Jesson, P. Meakin, and L. G. Glasgow, "The Fluorocarbon-Ozone Theory II: Tropospheric Lifetimes: An Experimental Estimate of the Tropospheric Lifetime of CCl_3F," accepted for publication in Atmos. Environ.

16. R. G. Prinn, F. N. Alyea, and D. M. Cunnold, Bull. Am. Meteorol. Soc. 57, 686-94, June, 1976.

measurements, Drs. J. E. Lovelock, R. A. Rasmussen, and D. H. Stedman. Two are investigating new methods of absolute calibration, and one will conduct an interlaboratory comparison program.

4. "Reduce errors in rate constants--Considerable improvement in the rate constants for the $Cl + CH_4$ and $HO + HO_2$ reactions should be sought and may be expected within the next year or two. Further work on several of the other reactions in Table 8.3 would serve to reduce their lesser contributions to the uncertainties. A strong effort should be made to reduce the uncertainty factor of the $HO + HO_2$ reaction to 1.5 and those of the other reactions to 1.3, or less, including the effects of temperature dependences."[17]

The uncertainty in the rate of the reaction $HO + HO_2$, of all the reactions in the model, accounts for the largest uncertainty in calculated ozone depletion. Because this is a reaction between two radicals, it is especially difficult to measure. The chlorofluorocarbon manufacturers are supporting two investigators to determine the rate of this and other reactions of the HO_2 radical Drs. B. A. Thrush of the University of Cambridge and C. J. Howard of the NOAA-Boulder laboratory. Dr. J. W. Birks has measured the rate of the reaction $ClO + NO_2$, which is listed as another of the important reactions in the NAS Panel report.

5. "Detailed evaluation of identified sinks--As a complement to the materials balance approach, inactive removal processes of CFMs, once identified, should be characterized in quantitative terms. In particular, oceanic removal of F-11 should be investigated more thoroughly by additional measurements of its concentration gradient in surface waters, by observations of its transport across the air-water interface, by redetermination of its solubility in sea water, and by a search for mechanisms that might contribute to its degradation in the surface waters. The same types of studies should be made for F-12. Also, efforts should be made to place narrower limits on the removal of F-11 and F-12 by photolysis and ion-molecule reactions in the troposphere."[18]

A number of potential sinks for the chlorofluorocarbons have been investigated in the industry sponsored program including photochemical changes by Dr. C. Sandorfy of the University

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17. Reference 1, page F-3.

18. Reference 1, page F-3.

of Montreal;[19] reactions with plants and soil and with OH and the $O(^1D)$ atom[20] by Dr. J. N. Pitts of the University of California at Riverside; reactions involving charged species by Dr. M. J. Campbell of Washington State University,[21] Dr. V. A. Mohnen of SUNY Albany, and Dr. R. G. Hirsch of Du Pont;[22] and trapping in Antarctic ice by Dr. R. A. Rasmussen. These projects have not identified with certainty a tropospheric sink for chlorofluorocarbons; studies by Dr. J. E. Lovelock are continuing.

f. "Improve other aspects of atmospheric chemistry--Photochemical processes and concentrations of natural species (NO_x and HO_x) contribute appreciable uncertainties to the prediction of ozone reduction by the CFMs. These aspects should be studied further, to place better limits upon their importance and to seek the most productive ways of reducing their contributions."[23]

OH is among the HO_x species contributing to the uncertainties in the prediction of ozone depletion by the chlorofluorocarbons. The industry is supporting development of an instrument by Dr. D. D. Davis for measuring stratospheric OH concentrations by laser-induced fluorescence. A miniturized version of a unit flown successfully earlier on an airplane is being prepared for balloon flights, which will allow observations over extended periods of time, and of diurnal changes.

In accordance with the NAS Panel recommendation that important species be measured simultaneously by two different methods, Dr. D. G. Murcray is also being supported to measure the concentration of stratospheric OH by solar ultraviolet absorption.

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19. C. Sandorfy, Atmos. Environ. 10, 343-51, May, 1976.

20. R. Atkinson, G. M. Brewer, J. N. Pitts, Jr., and H. L. Sandoval, "Tropospheric and Stratospheric Sinks for Halocarbons," accepted for publication in J. Geophys. Res.

21. M. J. Campbell, Geophys. Res. Lett. 3, 661-4, November, 1976.

22. R. G. Hirsch, Atmos. Environ. 10, 703-5, September, 1976.

23. Reference 1, pages F-3,4.

SUMMARY

Research Program on

EFFECT OF FLUOROCARBONS ON THE ATMOSPHERE

Sponsored by: The Fluorocarbon Industry

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1825 Connecticut Avenue, N. W.
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(Originally Issued: September 26, 1975)

Revision No. 5: December 31, 1976

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SUMMARY

Research Program on

EFFECT OF FLUOROCARBONS ON THE ATMOSPHERE

Sponsored by the Fluorocarbon Industry

Administered by the Manufacturing Chemists Association

(Originally Issued: September 26. 1975)
Revision No. 5: December 31, 1976

This summary describes work supported by the manufacturers of chlorofluorocarbons (commonly called fluorocarbons) in an attempt to assess the possible impact of these chemicals on the environment and, in particular, on the stratospheric ozone layer.

The Industry-Sponsored Program

In July of 1972, E. I. du Pont de Nemours & Company issued to fluorocarbon manufacturers worldwide an invitation to a "Seminar on the Ecology of Fluorocarbons." Its purpose was to establish a technical program because, as stated in the invitation,

> "Fluorocarbons are intentionally or accidentally vented to the atmosphere worldwide at a rate approaching one billion pounds per year. These compounds may be either accumulating in the

atmosphere or returning to the surface, land or sea, in the pure form or as decomposition products. Under any of these alternatives, it is prudent that we investigate any effects which the compounds may produce on plants or animals now or in the future."

Representatives of 15 companies attended the meeting, agreed that such a program was important, and established and funded a fluorocarbon research program under the administration of the Manufacturing Chemists Association (MCA). Thus, in 1972, with no evidence that fluorocarbons could harm the environment, the producers of these chemicals agreed unanimously that there was a need for more information and proceeded to act.

The 20 fluorocarbon producers supporting this program (see Table 1, p. 8) represent almost the total free world production of fluorocarbons. The research is directed by an MCA Technical Panel on Fluorocarbon Research with one member from each supporting company. This Technical Panel meets for two full days each month to review progress on current research, evaluate new proposals, and exchange data with contractors and with government agencies and researchers. Three projects were initiated in 1973:

1. Dr. James Lovelock, U. of Reading, "Fluorocarbons in the Environment."
2. Dr. Camile Sandorfy, U. of Montreal, "Spectroscopy and Photochemical Changes in Fluorocarbons."

3. Dr. O. C. Taylor, U. of California-Riverside, "Monitoring and Atmospheric Reactions of Fluorocarbons."

Publication of the Rowland-Molina hypothesis in 1974 identified a potentially serious problem, so the MCA research program was expanded considerably. The fluorocarbon-ozone relationship attracted the attention of many scientists in academic and government laboratories, legislative and regulatory bodies, and the press. MCA's program is concentrating on research most likely to answer the critical question: to what extent will fluorocarbons affect the stratospheric ozone layer?

To strengthen the overall effort to find the answer, MCA has attempted to coordinate its efforts with others working on the same or related problems such as the SST and the space shuttle. All of these concern the federal government, and interactions with a number of agencies have been especially helpful in:

1. Taking advantage of the knowledge and experience gained in the Climatic Impact Assessment Program;
2. Coordinating funding of programs addressing the halogen-ozone problem;
3. Planning joint experiments with government research groups; and
4. Helping to set priorities for industry-sponsored research.

About 165 research proposals have been reviewed to date, and projects totaling over $3,200,000 have been funded (see Table 2, p. 10). Calendar 1977 commitments are expected to exceed $2,000,000, with total expenditures through 1977 expected to exceed $5,000,000. Approximately $650,000 has been committed to studies concerning the measurement of reactive chlorine species in the stratosphere, a difficult and important area. A promising method was developed at the University of Michigan with MCA support, and funding for the follow-on program for development of equipment and stratospheric measurements has been provided by the National Aeronautics and Space Administration (NASA). This illustrates an important contribution by industry: prompt funding of promising work that, if successful, can be taken over by a government agency for incorporation into its more comprehensive program.

MCA Technical Panel members have visited knowledgeable scientists throughout North America and Europe, including many at government laboratories. The panel held its September 1975 meeting in Montreal where, in addition to hearing presentations by Canadian contractors and potential contractors, it was briefed on the stratospheric measurement program of the Canadian government. The February 1976 panel meeting was held near Milan, Italy, and the October 1976 meeting in Erbach, Germany. The panel was briefed on pertinent European activities and heard presentations by European atmospheric scientists at these meetings.

Discussions in early 1975 with the Energy Research and Development Administration's (ERDA) Sandia Laboratory at Albuquerque and the Army's Atmospheric Sciences Laboratory at White

Sands Missile Range, New Mexico, indicated that industry could contribute significantly to the stratospheric composition (STRATCOM) program. Cooperation began immediately with the panel providing funding for two additional STRATCOM experiments and an additional balloon for stratospheric measurements in the fall of 1975. Similarly, the panel provided funding for several experiments that were flown on balloons included in the May 1976 Army COSMEP flights in Alaska and the STRATCOM flights in September 1976. In the 1976 flights there was also cooperation between MCA contractors and the Atmospheric Environment Service of Canada on Fourier transform spectrometer measurements. Through these types of collaboration it is hoped to reduce substantially the time required to obtain critical research results.

Gaps in Scientific Knowledge

Two groups were charged during 1975 with looking exclusively at the scientific aspects of the halocarbon-ozone problem and making recommendations for further work. In May 1975 the government's Interdepartmental Committee for Atmospheric Sciences (ICAS) made 12 recommendations for research and monitoring programs to assess the possible impact of fluorocarbons and halogens on ozone. Six of these were singled out as of major importance. In July 1975 the Panel on Atmospheric Chemistry of the National Academy of Sciences (NAS) identified a number of areas in which relevant data are nonexistent, fragmentary, or insufficient and listed 19 high priority areas requiring study. The final report of the NAS Panel, which was issued in September 1976, contains six recommendations for pertinent studies that are expected

to be completed in the period of up to two years that its parent committee, the NAS Committee on Impacts of Stratospheric Change, recommends be allowed before a decision is made on the necessity for restrictive action. The Panel also made fifteen recommendations for longer range studies, many of which are relevant to the possible impact of halogens on ozone.

Table 3 shows the relationship between the latest NAS recommendations and the research program sponsored by the fluorocarbon manufacturers (pp. 10 and 12) and with the preliminary recommendations of NAS and those of ICAS (pp. 11 and 13). There is generally good agreement between the ICAS and NAS recommendations. In addition to other small differences, the former include some aspects of monitoring not in the latter, and the latter include photolysis studies and bromine chemistry not in the former. The second column of Table 3 lists the MCA-administered industry program. Its emphasis is overwhelmingly in the major areas recommended by the NAS Panel and ICAS. The industry-sponsored program, therefore, aims to fill in the most important gaps in existing scientific knowledge. The only major area not in the MCA program is acceleration of ozone monitoring, which can be accomplished more appropriately by governmental and international agencies. In addition, the MCA program includes work to correlate UV radiation reaching the ground with ozone measurements and to improve the statistical treatment of ozone data so that very small abnormal changes can be detected in a much shorter period of time than was previously believed possible.

More detail on the MCA program is given in Tables 4, 5A, and 5B. Table 4 (p. 14) lists summaries of the projects by type of research activity. Table 5A (p. 27) lists completed projects, and Table 5B (p. 28) lists active projects in chronological order of funding. Table 6 (p. 30) lists publications resulting from industry sponsored work. These important contributions have not always been recognized as industry-funded activity.

In addition to the work supported by the industry as a whole there are also studies underway in the laboratories of individual member companies who have staff scientists able to make significant contributions to the resolution of the problem. Examples are the modeling, reaction, and spectroscopic studies at Du Pont and the statistical analysis of ozone trends at Allied.

Summary and Recommendations

In 1972 the fluorocarbon manufacturers began supporting a program to investigate the effects of fluorocarbons on the environment. This program has been expanded greatly to help determine the extent, if any, to which these compounds may affect the stratospheric ozone layer. Industry and government-sponsored scientists working on the halogen-ozone problem have cooperated effectively. Continuation of this cooperation is essential, with special attention to providing periodically updated summaries of research priorities, programs, and results, together with critical analyses of the reliability and significance of the data. Such a program will produce most rapidly the information required for rational decision making.

Table 1

FLUOROCARBON MANUFACTURERS

represented on the

MCA TECHNICAL PANEL ON FLUOROCARBON RESEARCH

Akzo Chemie nv (Holland)

Allied Chemical Corporation (U.S.)

Asahi Glass Co., Ltd. (Japan)

Australian Fluorine Chemical Pty. Ltd. (Australia)

Daikin Kogyo Co., Ltd. (Japan)

E. I. du Pont de Nemours & Company, Inc. (U.S.)

Du Pont of Canada Limited (Canada)

Hoechst AG (West Germany)

Imperial Chemical Industries Limited (England)

I.S.C. Chemicals Ltd. (England)

Kaiser Aluminum & Chemical Corporation (U.S.)

Kali-Chemie Aktiengesellschaft (West Germany)

Mitsui Fluorochemicals Co. Ltd. (Japan)

Montedison S.p.A. (Italy)

Pennwalt Corporation (U.S.)

Racon Incorporated (U.S.)

Rhône-Poulenc Industrie (France)

Showa Denko K. K. (Japan)

Ugine Kuhlmann, Produits Chimiques (France)

Union Carbide Corporation (U.S.)

December 31, 1976

Table 2

FLUOROCARBON RESEARCH PROGRAM

Administered by
Manufacturing Chemists Association

FINANCIAL SUMMARY

	Completed Projects	Active Projects	Total
Chemical Reactions and Kinetics	$ 242,050	$ 351,600	$ 593,650
Analytical Methods	259,312	105,418	364,730
Tropospheric Measurement	169,107	339,846	508,953
Stratospheric Measurement	211,187	1,036,530	1,247,717
Modeling	147,652	285,005	432,657
Consulting	31,475	22,646	54,121
TOTAL	$1,060,783	$2,141,045	$3,201,828

December 31, 1976

Table 3

FLUOROCARBON-OZONE PROBLEM - RECOMMENDED STUDIES AND NCA PROGRAM

NAS Recommendations, September 1976[a,b]	NCA Supported Work: Completed	NCA Supported Work: In Progress
I.1. Establish role of $ClONO_2$ in the stratosphere.		Birks - U. of Illino Murcray - U. of Denv Timmons - Catholic U Wiesenfeld - Cornell
I.2. Verify the reliability of predicted ozone reductions. a. via ClO and Cl profiles simultaneously with HCl, O_3, etc. b. via decrease in total ozone column c. via changes in ozone profile	Davis - U. of Maryland[f] Ekstrom - Battelle Northwest Stedman - U. of Michigan[f] Young - Xonics, Inc.[f]	Davis - U. of Maryla Institute of Techn Howard - NOAA-Boulde Murcray - U. of Denv Nicholls - York U.[f] Parzen and Pagano - Science and Techno Foundation, Inc. Solomon - State U. Stony Brook
I.3. Develop an accurate materials balance for F-11 and F-12. a. Establish requirements for sensitivity, calibration, and accuracy. b. Define minimum observational program.	Lovelock - U. of Reading Manufacturers via NCA Rasmussen - Washington State U. Taylor - U. of California-Riverside	Eggleton - AERE Harw Lovelock - Private Murcray - U. of Denv Manufacturers via NC Rasmussen - Washingt Stedman - U. of Mich
I.4. Reduce errors in rate constants with emphasis on $Cl + CH_4$, $OH + HO_2$, $ClO + O$, $ClO + NO$, $ClO + NO_2$, $OH + HCl$, $Cl + O_3$		Birks - U. of Illino Howard - NOAA-Boulde Thrush - U. of Cambr Timmons - Catholic Wiesenfeld - Cornell
I.5. Make a detailed evaluation of sinks once they are identified. a. Oceanic removal of F-11 and F-12. b. Photolysis of F-11 and F-12. c. Ion-molecule reactions of F-11 and F-12 in the troposphere.	Campbell - Washington State U. Mohnen - State U. of N.Y.-Albany Pitts - U. of California-Riverside	Birks - U. of Illino Kaufman - Emory U. Lovelock - U. of Rea Martin - Aerospace Rasmussen - Rasmuss
I.6. Improve other aspects of atmospheric chemistry. a. Photochemical processes of natural species (NO_x, HO_x). b. Concentrations of natural species.		Buijs - Bomem, Inc. Davis - U. of Maryla Institute of Techn Girard - ONERA (Fran Murcray - U. of Denv
II.1. Monitor all major releases of volatile halocarbons and other potential stratospheric pollutants on a global scale.	Lovelock - U. of Reading Rasmussen - Washington State U. Taylor - U. of California-Riverside	Lovelock - Private Murcray - U. of Denv Rasmussen - Washingt Ridley - York U.
II.2. Determine sinks for every substance identified as a potential or actual hazard to the stratosphere.		cf. I.5
II.3. Determine for each pollutant the complete sequence of events from injection to removal of the final products from the atmosphere. a. Fate of halocarbon radicals remaining after photodissociation. b. Effect of HF and HCl on rain and snow.		
II.4. Improve reliability of 1-D calculations. a. More extensive and more accurate data for CH_4, N_2O, HF, and O_3 for "fine-tuning" models. b. Treatment of diurnal variations.		Cunnold, Alyea, Prin ates Sze - ERT, Inc.
II.5. Expedite development of 2- and 3-D models.		Cunnold, Alyea, Prin ates
II.6. Determine accurate rate constants for a large number of chemical reactions involving ClX and atmospheric species, HO_x chemistry, and $O(^1D)$ quenching and reaction rate constants.		cf. I.4
II.7. Determine reaction rate parameters over the tropospheric and stratospheric temperature range for the reaction of OH with all important chloro- and fluorocarbons.		

ICAS Recommendations, May 1975[c,d]	NAS Recommendations, July 1975[e]
1. Measure Cl and ClO concentrations in the stratosphere. 5. Accelerate program for monitoring of ozone on a global basis. Establish trends in atmospheric ozone.	1. Measure Cl and ClO upper atmosphere concentration profiles.
3. Make systematic search for other chlorine-bearing gases in the stratosphere. A2. Expand monitoring of F-11, F-12, and CCl_4 in the troposphere and develop standards for their measurement.	14. Determine total chlorine in the atmosphere and compare with sum of all identified compounds.
6. Confirm and improve certain reaction rate measurements crucial to ozone destruction.	6. Measure rate constants for $ClO + NO$, $ClO + O$, $Cl + HO_2$, $Cl + CH_4$. 7. Measure rate constants for $OH + H_2O$; H, O, NO, $O_3 + HO_2$; H_2O, CH_4, N_2, $O_2 + O(^1D)$.
4. Conduct promising research to determine sinks for chlorine in the stratosphere.	16. Seek out and characterize other possible sinks for removal of chlorofluorocarbons. 17. Determine source and further reactions of chlorine in stratospheric particulates.
2. Measure [F-11, F-12, CCl_4, HOH, H_2O, and other gases at 25-40 km.	2. Measure OH, HCl, HF, NO, etc., upper atmosphere concentration profiles. 12. Sample at low altitude to find additional possible natural and anthropogenic sources of halogen-containing compounds. Establish concentrations.
2. Measure F-11, F-12, CCl_4, [OH, H_2O,] and other gases at 25-40 km. A1. Obtain a full record of past and present halocarbon production and release.	4. Measure F-11, F-12, CCl_4, $CHCl_3$, and N_2O concentration profiles 0-40 km Establish standards. 13. Obtain accurate data on production and uses of each halocarbon manufactured worldwide.
Cf. I.3 A3. Study the lifetimes of halocarbons, HCl, and phosgene in the troposphere.	Cf. I.5
	15. Measure atmospheric abundance of decomposition products such as COF_2, $COCl_2$, COFCl, and determine whether COFCl releases additional Cl.
A4. Expand the stratospheric modeling studies of ozone formation and destruction. Improve chemistry and transport.	3. Measure global distribution of certain trace gases to improve models. 5. Develop better atmospheric models.
	Cf. II.4
Cf. I.4	Cf. I.4
Cf. I.4	8. Measure rate constants for $OH + CH_2FCl$, CHF_2Cl, CH_3Cl, CH_3CCl_3, CH_2Cl_2, and all other potentially usable halocarbons with C-H bonds.

(continued)

Table 1 (continued)

NAS Recommendations, September 1976[a,b]	MCA Supported Work	
	Completed	In progress
II.8. Determine kinetic data for all important reactions of BrX and photolytic properties of the various bromine-containing species.		
II.9. Measure solar flux and its variability, especially at wavelengths greater than 175 nm, and stratospheric scattering parameters.		
II.10. Study photochemistry of halocarbons and ClX further. a. Photolysis parameters of F-11, F-12, OClO, ClOO, $ClNO_2$, and $ClONO_2$. b. Photolysis parameters of other halocarbons such as $CHFCl_2$, CCl_4, CH_3CCl_3, CH_2Cl_2, and CH_3Cl.	Sandorfy - U. of Montreal	
II.11. Define and establish a global network for atmospheric measurements.	Ekstrom - Battelle Northwest	Solomon - State U. of N. Y. - Stony Brook
II.12. Measure concentration profiles in upper atmosphere for species related to the chemistry of chlorine, including OH, HCl, HF, and NO.		Butjs - Bomem, Inc. Davis - U. of Maryland/Georgia Institute of Technology Girard - ONERA (France)[g] Murcray - U. of Denver
II.13. Make global monitoring of ozone sufficiently sensitive, accurate, and complete to detect small changes due to man's activities.		Parzen and Pagano - Frontier Science and Technology Research Foundation, Inc.
II.14. Give further attention to the problem of water vapor feedback.		
II.15. Study the reduction in stratospheric ozone associated with the use of nitrogen fertilizers including the effects of the interaction between the NO_x and ClO_x cycles.		
		Cunnold, Alyea, Prinn - CAP Associates
	Nicholls - York U.	Davis - U. of Maryland/Georgia Institute of Technology

a. "Halocarbons: Effects on Stratospheric Ozone," Panel on Atmospheric Chemistry, Committee on Impacts on Stratospheric Change, Assembly of Mathematical and Physical Sciences, National Research Council, NAS, September, 1976, Appendix F.

b. Group I items are short-term (1-2 year), Group II longer range.

c. "The Possible Impact of Fluorocarbons and Halocarbons on Ozone," ICAS 18a-FY 75, May, 1975, pp. 64-66.

d. 1-6 indicate major recommendations, A1-A6 other.

e. "Interim Report of the Panel on Atmospheric Chemistry," Climatic Impact Committee, Assembly of Mathematical and Physical Sciences, National Research Council, NAS, July, 1975, pp. 1-8.

f. Laboratory study to develop data, analytical method, or instrumentation required for stratospheric measurements.

g. Office National d'Etudes et de Recherches Aérospatiales.

S Recommendations, May 1975[c,d]	NAS Recommendations, July 1975[e]
	19. Obtain kinetic data for all important reactions of bromine, Br + O_3, HO_2; BrO + O, NO, O_3; CH_3Br + OH.
	9. Measure solar flux and scattering parameters for the stratosphere.
	10. Measure photolysis parameters for chlorohydrocarbons and chlorofluorocarbons.
Expand monitoring of F-11, F-12, and CCl_4 in the troposphere [and develop standards for their measurement].	18. Accurate baseline monitoring of ground level composition and absorption spectrum of "clean air" including measurements of O_3, HCl, HF, N_2O, NO, NO_2; monitoring of column densities of HCl, HF, ClO, OH, NO_2, O_3 from ground level and satellite stations.
I.6 and II.1	Cf. I.6, II.11
I.2	Cf. I.2
Expand the general circulation modeling of the effects of reduced stratospheric ozone in climate.	
Continue to study the effects of releasing halocarbons on humans and the biosphere.	
	11. Make laboratory studies of the photolysis of ClO.

December 11, 1975

Table 4

Fluorocarbon Research Program

Types of Research Activities, Summaries

A. Reaction Rate Constant Measurements

Dr. J. W. BIRKS -- University of Illinois -- 75-1, 76-117A. Measurement of Reaction Rates Relevant to the Fluorocarbon-Ozone Problem.

Reaction rates are measured at various temperatures by a discharge flow technique with a quadrupole mass spectrometer for detection of products. Reactions studied include $ClO + O_3 + M$ (yields OClO, unimportant in daytime), $ClO + NO_2 + M$ (important in lower stratosphere, $k = 1.5 \times 10^{-13} cm^6\ molecule^{-2} s^{-1}$ at 297°K), $ClO + SO_2$ (no appreciable reaction observed), $NO + O_3$ (in agreement with previous studies), $O + ClONO_2$ (preliminary results in agreement with Davis), and $BrO + NO_2$ (in progress). The products of the four-center reactions $Cl_2O + Cl$, O, N, or ClO have been investigated by molecular beam mass spectrometry and indicate that O, N, and ClO all react with the O in ClOCl. Future work will include $ClO + H_2O_2$ and reactions of HO_2.

Dr. C. J. HOWARD -- NOAA Boulder -- 76-100. Laser Magnetic Resonance Study of HO_2 Chemistry.

The object of this study, which is just getting under way, is to use the laser magnetic resonance technique to measure rate constants for stratospherically important HO_2 reactions.

Dr. J. N. PITTS -- University of California at Riverside -- 74-2. Atmospheric Reactions of Fluorocarbons.

Reaction rate constants have been measured for the reactions of $O(^1D)$ with fluorocarbons 11, 12, 22, 113, and 114, and of OH with fluorocarbons 11, 12, and 22. The results indicate that in the stratosphere the reaction of $O(^1D)$ atoms with fluorocarbons 11 and 12 is secondary to photolysis, whereas the reaction of OH with fluorocarbon 22 is much more important than photolysis. The photooxidation products of 12, 13, and 22 at 184.9 nm, i.e., $COCl_2$, COFCl, and COF_2 as appropriate, are also observed to be the products for reaction with $O(^1D)$.

Table 4 (continued)

Dr. B. A. THRUSH -- University of Cambridge -- 75-58, 75-58II. Reactions of the HO_2 Radical Studied by Laser Magnetic Resonance.

The rate coefficient of the reaction O + HO_2 has been measured for the first time. The value found, 4.3×10^{-11} cm^3s^{-1}, improves the fit of the calculated OH profile with Anderson's recent measurements. Work on the HO + HO_2 reaction is in progress.

Dr. R. B. TIMMONS -- Catholic University -- 76-129. Photochemical and Chemical Kinetics Measurements of Stratospheric Importance With Respect to the Fluorocarbon Issue.

It is planned to measure accurately the UV absorption cross-section of HOCl, study its photochemistry, and perform $ClONO_2$ photochemical studies to complement Wiesenfeld's proposal (q.v., below). HOCl is a possible stratospheric sink the magnitude of which would depend on the absorption cross-section. Earlier spectral measurements were inaccurate.

Dr. J. WIESENFELD -- Cornell -- 76-128. Photochemistry of Small Chlorinated Molecules.

The photochemistry of chlorine nitrate will be studied. While not yet thoroughly treated in the models, chlorine nitrate may be an important stratospheric sink. A flash photolysis-resonance absorption system is used for photolysis and analysis of products and incorporates either a conventional flash lamp with filters or a tunable laser. The wavelength and temperature dependencies of the quantum yield and product formation will be determined.

B. Source and Sink Studies

Dr. J. W. BIRKS -- University of Illinois -- 76-117B. Studies of Heterogeneous Reactions.

Potentially important heterogeneous reactions, which will be chosen with the advice of ERT, are to be studied, including the heterogeneous reaction of $ClONO_2$ and H_2O. Equipment is being assembled for measurements in early 1977.

Table 4 (continued)

Dr. M. J. CAMPBELL -- Washington State University -- 75-53. Chlorofluoromethane Destruction by Natural Ionization.

Laboratory measurements under conditions approximating the real atmosphere in all respects except ion age show large rate constants for removal of CCl_4 and fluorocarbon 11, apparently by atmospheric ions. The rate constant for fluorocarbon 12 is much smaller. If the same rate constants were to hold for older ions, this mechanism might constitute a sink that could decrease the stratospheric concentration of fluorocarbon 11 by a factor of two.

Dr. M. KAUFMAN -- Emory University -- 76-126. Studies of Compounds of Sulfur, Oxygen, and Chlorine.

Reactions between SO_x and Cl_x species of possible stratospheric importance are being investigated. They may yield compounds with long lifetimes or lead to incorporation of Cl into aerosols. Currently, the rate constant of the reaction of Cl with SO_2 is being measured.

Dr. J. E. LOVELOCK -- University of Reading -- 75-67. Unidentified Factors in the Fluorocarbon-Ozone Problem.

The absorption and reactivity characteristics of the atmospheric dust plume from the Sahara for atmospheric halocarbon vapors (fluorocarbon 11 and CCl_4) are being evaluated. Investigations are in progress on the relationship between photochemically produced atmospheric peroxy compounds (e.g., peroxyacetyl nitrate) and the incidence of skin carcinoma.

Dr. L. R. MARTIN -- Aerospace Corp. -- 75-81. Laboratory Investigation of the Heterogeneous Interaction of Cl and ClO With H_2SO_4.

A flowing afterglow apparatus is being used to measure the rate of the heterogeneous reactions of Cl and ClO with sulfuric acid, simulating the stratospheric aerosol. Preliminary data suggest that the reaction rate of Cl is too slow for its reaction to constitute a significant sink, although rates were markedly increased by the presence of certain metal salts in the sulfuric acid. Measurements of the ClO rates, to which the ozone depletion cycle is more sensitive, are planned. The nature of the surface interaction is also to be characterized.

Table 4 (continued)

Dr. V. A. MOHNEN -- SUNY Albany -- 75-64. Ion Molecule Reactions Involving Fluorocarbons.

A drift tube in which ions are formed and their mobility determined and an electric quadrupole mass spectrometer were used to study the role of ion-molecules in the reactions between fluorocarbon 12 and positive and negative ion clusters that form in air-like gas mixtures. There was no clustering of fluorocarbon 12 and no evidence for charge transfer or cluster ion reactions with positive ions of the form $H^+ \cdot (H_2O)_n (NH_3)_m$. Reaction with negative ions of the form $O^- \cdot X$ and $CO_4^- \cdot X$ results in the formation of the ion-cluster series $Cl^- \cdot (H_2O)_x$.

Dr. J. N. PITTS -- University of California at Riverside -- 75-12. Monitoring and Atmospheric Reactions of Fluorocarbons.

Long-term photolysis studies in simulated sunlight revealed that fluorocarbons 11 and 12 are photochemically stable, even when irradiated for several weeks. An attempt to study fluorocarbon-NO_x-air mixtures under simulated stratospheric conditions could not be completed because the background level of hydrocarbons in the environmental chamber could not be made sufficiently small.

Plant tissues did not absorb measurable quantities of fluorocarbons 11, 12, or 22, and no adverse effects could be measured. Fluorocarbons penetrate into the soil atmosphere, and concentrations change in direct relationship with changes in concentration in the atmosphere above ground.

Dr. R. A. RASMUSSEN -- Washington State University -- 75-71. Measurement of Fluorocarbon Content of "Antique" Air Samples.

A sensitive method for the determination of low parts per trillion analysis of fluorocarbons 11 and 12 in small-volume air samples in containers was developed and applied to a wide variety of vessels believed to contain antique air. Both of these fluorocarbons were found in all samples analyzed, suggesting either the presence of natural fluorocarbons before 1930 or contamination during storage or handling.

Dr. R. A. RASMUSSEN -- Washington State University -- 75-84. Collection and Analysis of Antarctic Ice Cores.

The concentration of halocarbons in air obtained from Antarctic snow shows no enrichment in samples obtained from the Ross ice shelf (mainly -30°F), whereas there is enrichment in samples obtained from the South Pole (-50 to -60°F).

Dr. R. A. RASMUSSEN -- Private -- 76-140. Lower Stratospheric Measurement of Non-methane Hydrocarbons.

This study is now beginning. It is important because non-methane hydrocarbons, if present in the stratosphere, will act as a sink for Cl in the same way that methane acts and thus reduce the ozone depletion attributable to chlorine-containing species.

Dr. C. SANDORFY -- University of Montreal -- 73-2. Spectroscopy and Photochemical Changes of Fluorocarbons.

The vacuum ultraviolet and photoelectron spectra of all industrially important chlorofluorocarbons were measured and published. The photochemical vulnerability of these molecules was predicted from their spectra.

C. Laboratory Studies Related to Potential Atmospheric Measurements

Dr. H. J. BUIJS -- Bomem, Inc. -- 75-90. Construction of a Fourier Transform Spectrometer.

A spectrometer with a projected resolution of 0.01 cm^{-1} is being completed for use in the simultaneous determination of $ClONO_2$ and either HCl or HF, or of HCl and HF.

Dr. D. D. DAVIS -- University of Maryland -- 74-10. Laboratory Determination of the Sensitivity of Laser-Induced Fluorescence for the Detection of ClO Under Atmospheric Conditions.

Ground-state stationary ClO concentrations of about $10^{12} cm^{-3}$ were scanned at several electronic absorption wavelength regions with a tunable UV laser. Laser-induced fluorescence proved to be unusable for measuring ClO because (1) at 300°K the highest populated K level, 12, contains only 5% of the total ClO and (2) the majority of the ClO undergoes predissociation to Cl and O.

Table 4 (continued)

Dr. D. D. DAVIS -- University of Maryland/Georgia Institute of Technology -- 75-73. Laboratory Measurement of Spectroscopic Absorption Cross-Sections of ClO.

Work is being completed on the measurement of the absorption cross-sections for ClO, data required for determining concentrations from UV absorption measurements of this molecule.

Dr. D. D. DAVIS -- University of Maryland/Georgia Institute of Technology -- 75-87. Development of Instrument for Stratospheric OH Measurement by Laser-Induced Fluorescence.

This program is to measure stratospheric OH concentrations over extended periods of time, including some covering diurnal changes. A miniaturized dye laser module for balloon flights has been built and tested. An engineering flight is planned after a high-altitude, pressurized chamber for housing the dye laser and Nd-Yag driver has been built and required data storage and control facilities are ready.

Dr. A. E. J. EGGLETON -- AERE Harwell -- 76-116. Total Chlorine Measurements in the Troposphere and Stratosphere.

The feasibility of measuring total chlorine and fluorine in the atmosphere by neutron activation and γ photon activation, respectively, after collection of reactive species and particulate material on a filter and collection of gaseous compounds on activated charcoal is being studied.

Dr. C. J. HOWARD -- NOAA, Boulder -- 75-47. Laboratory Determination of the Feasibility of Laser Magnetic Resonance for ClO Detection and Reaction Studies.

This study is to detect ClO using laser magnetic resonance and to utilize this method for measuring rate constants for stratospherically significant ClO reactions. It has been demonstrated that ClO can be detected by this method, and the sensitivity is under evaluation.

Dr. J. E. LOVELOCK -- Private -- 76-120. The Electron Capture Detector as a Reference Standard for Analysis of Atmospheric Halocarbons.

The electron capture gas chromatograph is being investigated as a reference standard for analysis of atmospheric halocarbons.

Table 4 (continued)

Dr. D. G. MURCRAY -- University of Denver -- 75-92. Laboratory Measurement of High Resolution Infrared Spectra of Chlorine-Containing Molecules of Stratospheric Interest.

Laboratory measurements of the high resolution infrared spectra of chlorine-containing molecules are to be made. Statistical-band-model analyses and integrated intensity measurements for the 10.8 μm band of fluorocarbon 12 and 11.8 μm band of fluorocarbon 11 have been published. Additional spectra for methane, methyl chloride, and carbonyl fluoride have been run, and work is in progress on chlorine nitrate.

Dr. R. W. NICHOLLS -- York University -- 75-11 and 75-11-II. Experimental and Theoretical Studies on the UV Spectrum of ClO With Stratospheric Applications.

Absolute absorption coefficients and cross-sections have been measured for all bands and the photodissociation continuum of the V"=0 progression for ClO. The very complicated emission spectrum that has been excited over the wavelength range 2500-4500 Å in discharges through ClO_2 and Cl_2O is currently undergoing measurement, identification, and analysis. Computer-based synthetic spectra of various ClO bands have been calculated. Emphasis is now being placed on the high resolution spectrum of ClO in the spectral region above 3000 Å, which should lay the groundwork for the detection and measurement of stratospheric ClO from the ground and from balloon-borne equipment. Possible interferences by O_3 are being evaluated.

Dr. R. W. NICHOLLS -- York University -- 75-30b. Laboratory Studies of the Infrared Vibration-Rotation Spectrum of ClO.

Work in this area was suspended to allow greater effort in the UV measurements (75-11).

Dr. R. A. RASMUSSEN -- Private -- 76-142. Interlaboratory Comparison of Fluorocarbon Measurements.

A second round of identical samples of rural air will be circulated blind to participating laboratories for analysis for fluorocarbons 11 and 12, chloroform, methyl chloroform, carbon tetrachloride, and N_2O. The results will be analyzed statistically.

Dr. D. H. STEDMAN -- University of Michigan -- 74-7. Atmospheric Determination of ClO Concentration: A Feasibility Study.

Laboratory studies have demonstrated the feasibility for detecting stratospheric ClO by chemical conversion to Cl (by reaction with NO) accompanied by vacuum ultraviolet resonance fluorescence. In-flight use of this technique is being supported by NASA.

Dr. D. H. STEDMAN -- University of Michigan -- 76-132. Absolute Calibration of Fluorocarbon Measurements.

The final design of a feed-back flow system for the calibration of fluorocarbon samples is being built.

D. Tropospheric and Stratospheric Measurements

Dr. H. L. BUIJS -- Bomem, Inc. -- 75-98. Measurement of HCl and HF in the Stratosphere by Fourier Transform Spectroscopy.

Data have been successfully collected from balloon flights in Alaska (May 1976) and New Mexico (September 1976) and are being analyzed for HCl and HF concentrations.

Dr. P. A. EKSTROM -- Battelle Memorial Institute, Pacific Northwest Laboratories -- 75-27. Ground-Based Millimeter-Wavelength Observations of Stratospheric ClO.

About 500,000 data points were obtained in the microwave spectra near 93 GHz with the Kitt Peak radiotelescope. Excessive noise made interpretation difficult, but base-line corrected spectra suggested an upper limit on ClO of one hundred times model predictions.

Dr. A. GIRARD -- ONERA - France -- 75-88. Measurement of HCl, HF, ClO, etc., in the Stratosphere by High Resolution Infrared Spectroscopy.

Balloon-borne flights and supporting laboratory work are planned to measure fluorocarbons, HCl, HF, ClO, $ClNO_3$, and other compounds by high resolution infrared spectroscopy. This program is part of a cooperative program including aircraft flights with the Centre National d'Etudes Spatiales. A flight in 1976 provided an HCl concentration profile between 25 and 30 km. Equipment failure occurred in a September 1976 flight. A flight from Brazil in December 1976 and additional flights in the spring of 1977 are planned.

Table 4 (continued)

Dr. J. E. LOVELOCK -- University of Reading -- 73-1, 74-3, 75-67. Fluorocarbons in the Environment.

The electron-capture gas chromatograph (ECGC) has been developed and applied to the measurement of chlorocarbons and chlorofluorocarbons in the troposphere and lower stratosphere, particularly over Europe and the Atlantic Ocean. Current fluorocarbon 11 levels are about 130 ppt (U.K.) and 80 ppt (Southern Hemisphere). ECGC has been adapted to measure CH_3Cl at atmospheric concentrations of about 10^{-9} v/v, with sources for CH_3Cl identified as the ocean and smouldering vegetation.

Dr. D. G. MURCRAY -- University of Denver -- 75-13, 76-101, 76-135. The Measurement of the Stratospheric Distribution of Fluorocarbons and Other Constituents of Interest in the Possible Effect of Chlorine Pollutants on the Ozone Layer.

Measurement of stratospheric distribution by balloon-borne, high-resolution, infrared absorption measurement at large solar zenith angles has been achieved using a specially-constructed grating spectrometer. The distributions for fluorocarbon 11, fluorocarbon 12, and CCl_4 obtained show a concentration increase of about 2.5, with a rather wide range of uncertainty, from 1968 to 1975 for fluorocarbon 11 and fluorocarbon 12. Subsequent flights also yielded HCl and HNO_3 profiles. Profiles or upper limit measurements on several other species, including $ClONO_2$, are potentially accessible.

Balloon-borne experiments will be continued to measure stratospheric ClO (300-500 nm) and OH (306.4 nm) by solar UV absorption.

Dr. R. A. RASMUSSEN -- Washington State University -- 75-2, 75-59. Fluorocarbon Research.

An attempt was made to obtain halocarbon concentration measurements as far into the stratosphere as could be reached by an available commercial aircraft. A small portable gas chromatograph was used for on-board measurements, and cannister samples were collected for subsequent detailed halocarbon analysis on the ground. One phase of the study consisted of samples collected over a wide area of the Pacific Northwest, a second of samples collected frequently to the maximum attainable altitude over Alaska. The halocarbon

Table 4 (continued)

concentrations are either constant or decrease very slowly with altitude in the troposphere, decrease rapidly in the tropopause from the tropospheric concentration to an average value identifiable with the stratosphere, and do not show a clear pattern of concentration gradients above the tropopause.

A trans-Pacific flight from 80°N to 60°S has been completed, and the air samples collected have been analyzed for halocarbons. Most of the samples were collected at 39,000 to 43,000 ft. Fluorocarbon 12 concentrations are about 10% higher in the north than in the south at ground level, and the difference is apparently greater for fluorocarbon 11.

Dr. B. A. RIDLEY -- York University -- 76-102A, 76-102B. Measurement of Fluorocarbons and Related Chlorocarbons in the Stratosphere by Collection and Analysis.

Balloon-borne grab sample devices have been developed and flown to obtain fluorocarbon 11, fluorocarbon 12, and N_2O concentrations at 10-40 km altitude. The data show a relatively consistent drop-off with height above the tropopause, whereas their consistency in drop-off is much worse as a function of height above the surface. The spread in data is larger than the accuracy of the measurements, which indicates variability in stratospheric concentrations due to horizontal motions.

Dr. P. M. SOLOMON -- SUNY Stony Brook -- 76-130. Millimeter Wave Observations of Chlorofluoromethane Byproducts in the Stratosphere.

This study, which is directed toward the development of a ground-based method for continuous determination of ClO, is just getting under way. One of the millimeter wave observing systems will be based on a 3 mm maser, a unique instrument that is the most sensitive detector in the world in the 83-94 GHz range.

Dr. O. C. TAYLOR -- University of California at Riverside -- 73-3, 74-2. Monitoring and Atmospheric Reactions of Fluorocarbons.

An electron capture gas chromatograph was used to measure the concentrations of fluorocarbons 11 and 12 in the troposphere over southern California and in the lower stratosphere over New Mexico and Colorado. The tropospheric concentrations were found to

vary from day to day as climatic conditions affected dispersion and dilution. Concentration decreased with increasing altitude in the lower stratosphere.

Dr. R. A. YOUNG -- Xonics, Inc. -- 75-50, 75-86. Development of an Instrument to Measure O, ClO, O_3, and Total Cl in the Stratosphere.

The preliminary experiment to measure stratospheric ClO and total chlorine by resonance fluorescence flown on the September 1975 STRATCOM balloon was not completely successful; however, several key components appeared to have functioned satisfactorily. Follow-up work has been undertaken in a stratospheric simulator to provide design information for further development of stratospheric instrumentation.

E. Modeling

Drs. D. M. CUNNOLD, F. N. ALYEA, and R. G. PRINN -- CAP Associates -- 75-24, 76-122, 76-122S. Meteorological and Multi-Dimensional Modeling Considerations Relating to Atmospheric Effects of Halocarbons.

Studies to assess the accuracy and shortcomings of the 1-D model used to estimate ozone depletion indicated that a tropospheric lifetime for fluorocarbons 11 and 12 as short as 10 years was not inconsistent with atmospheric measurements. Thus, ozone depletion estimates might be considerably less than present estimates. The great variability of stratospheric measurements indicates that simultaneous measurements for many important stratospheric species are needed and that seasonal dependence of species must be considered.

The absence of circulation in the radiative models used to calculate warming (greenhouse effect) limits the value of calculated effects.

Because it has been shown that meteorological conditions can cause variations in both tropospheric and lower stratospheric fluorocarbon measurements in Alaska, meteorological analysis will be performed for selected fluorocarbon measurements, and temporal and latitudinal variability of fluorocarbon concentration will be determined using 2-D and 3-D models.

Table 4 (continued)

Dr. N. D. SZE -- Environmental Research and Technology, Inc. -- 75-32, 76-115. Model Analysis of the Fluorocarbon Problem.

A one-dimensional model has been used to evaluate the role of stratospheric water in the NO_x and ClX cycles, the relationship of eddy diffusion coefficient and fluorocarbon lifetime, the use of fluorocarbon measurements to calculate lifetime, and the effect of chlorine nitrate. The importance of OH concentration on calculated ozone depletion was shown, and key reactions were identified. Analyses showed 10-20 year tropospheric lifetimes were not inconsistent with measurements and helped to define quantitatively the uncertainties associated with ozone depletion calculations. Current work is to continue a sensitivity analysis of the 1-D model, develop a diurnal 1-D model, and include multiple scattering and heterogeneous (aerosol) reactions in the model.

F. Other

Dr. D. BERGER - Temple University -- 75-62. Ground-Level Monitoring of Ultraviolet Solar Radiation.

The monitoring of solar ultraviolet radiation, initiated by the Climatic Impact Assessment Program (CIAP), is being continued. The number of instruments and stations is being increased. Calibration of operating instruments is maintained, and comparisons between different types of monitoring equipment are being made.

Drs. E. PARZEN and M. PAGANO -- Frontier Science and Technology Research Foundation, Inc. -- 76-106. Total World Ozone Level: Statistical Analysis.

Ozone column measurements from at least 20 stations are being evaluated statistically to detect trends in recorded ozone concentrations and to establish the limits of detection for such trends. Time series analysis has been shown to be substantially more sensitive in detecting non-random ozone changes than the estimates of such sensitivity made by the Federal Task Force on Inadvertent Modification of the Stratosphere (IMOS) in 1975. The absence of detectable trends provides an upper limit for actual depletion and a test of model predictions.

Table 4 (continued)

If sufficient sensitivity is achieved, this technique will enable an effective early warning system for ozone depletion to be established.

G. Consultants

Dr. J. G. Anderson	University of Michigan	Stratospheric Measurements
Dr. A. W. Castleman, Jr.	University of Colorado	Heterogeneous Chemistry
Dr. F. C Fehsenfeld Dr. E. F. Ferguson	NOAA Environmental Research Laboratories	Reactions of Charged Specie
Dr. D. R. Herschbach Dr. W. Klemperer	Harvard University	Homogeneous Chemistry, Kir and Spectrosco
Dr. L. E. Snyder	University of Illinois	Millimeter Wav length Spectro copy

December 11, 19

Table 5A

Research Funded by the Fluorocarbon Industry
and
Administered by the Manufacturing Chemists Association

WORK COMPLETED

Program	Investigator	Organization	Proposal Number	Completion Date
Measurement of fluorocarbons in the atmosphere*	Lovelock	U. of Reading	73-1	10/27/74
Monitoring of fluorocarbons in the atmosphere and simulation of atmospheric reactions of fluorocarbons	Taylor	U. of Calif.-Riverside	73-3	10/16/74
Investigation of spectroscopy of and photochemical changes in fluorocarbons	Sandorfy	U. of Montreal	73-2	10/11/74
Continuation of 73-1*	Lovelock	U. of Reading	74-3	12/31/75
Laboratory determination of sensitivity of laser-induced fluorescence for the detection of ClO under atmospheric conditions	Davis	U. of Maryland	74-10	5/31/75
Laboratory investigation of the feasibility of measuring ClO in the atmosphere by the chemical conversion-resonance fluorescence detection method	Stedman	U. of Michigan	74-7	2/28/75
Continuation of 73-3	Pitts	U. of Calif.-Riverside	74-2	12/31/75
Measurement of fluorocarbons and related chlorocarbons in the stratosphere and upper troposphere*	Rasmussen	Washington State U.	75-2	4/15/76
Laboratory and theoretical studies of the ultraviolet and visible electronic spectra of ClO*	Nicholls	York U.	75-11	6/14/76
Continuation of 74-2	Pitts	U. of Calif.-Riverside	75-12	4/15/76
Ground-based millimeter wavelength observations of stratospheric ClO	Ekstrom	Battelle Northwest	75-27	5/24/76
Investigation of the destruction of chlorofluoromethanes by naturally occurring ions	Campbell	Washington State U.	75-53	4/23/76
Development of an instrument to measure O, ClO, O_3, and total Cl in the stratosphere	Young	Xonics, Inc.	75-50	4/7/76
Investigation of ion-molecule reactions involving chlorofluorocarbons	Mohnen	State U. of N.Y.-Albany	75-64	4/1/76
Modeling of the fluorocarbon-ozone system*	Sze	ERT, Inc.	75-32	8/18/76
Critique of models used to estimate chlorofluorocarbon effects on ozone*	Cunnold, Alyea, Prinn	CAP Associates	75-24	9/10/76
Studies of reactions of HO_2 by laser magnetic resonance*	Thrush	U. of Cambridge	75-58	11/8/76
Continuation of 75-50	Young	Xonics, Inc.	75-86	11/15/76

*Work is continuing in a follow-on contract.

December 31, 1976

Table 5B

Research Funded by the Fluorocarbon Industry
and
Administered by the Manufacturing Chemists Association

WORK IN PROGRESS

Program	Investigator	Organization	Proposal Number	Contract Date	Contract Period
Measurement of reaction rates relevant to the fluorocarbon-ozone problem	Birks	U. of Illinois	75-1	4/17/75	15 mo.[a]
Measurement of stratospheric distribution of fluorocarbons and related species by infrared absorption spectroscopy	Murcray	U. of Denver	75-13	6/16/75	12 mo.[a]
Laboratory studies of the infrared vibration-rotation spectrum of ClO	Nicholls	York U.	75-30b	8/12/75	12 mo.[a]
Laboratory determination of the feasibility of laser magnetic resonance for ClO detection and reaction studies	Howard	NOAA-Boulder	75-47	11/13/75	12 mo.[a]
Collection and analysis of Antarctic ice cores	Rasmussen	Rasmussen Associates	75-84	11/29/75	3 mo.[a]
Measurement of fluorocarbon content of "antique" air samples	Rasmussen	Washington State U.	75-71	12/3/75	5 mo.[a]
Exploration for unidentified factors in the fluorocarbon-ozone problem	Lovelock	Private	75-67	12/4/75	12 mo.[a]
Laboratory measurement of spectroscopic absorption cross sections of ClO	Davis	U. of Maryland	75-73	2/5/76	8 mo.[a]
Continuation of program for ground level monitoring of ultraviolet solar radiation	Berger	Temple U.	75-62	2/5/76	12 mo.
Continuation of 75-2	Rasmussen	Washington State U.	75-59	2/13/76	9 mo.[a]
Measurement of OH in the stratosphere by laser induced fluorescence	Davis	U. of Maryland	75-87	2/24/76	12 mo.
Laboratory measurement of high resolution infrared spectra of chlorine-containing molecules of stratospheric interest	Murcray	U. of Denver	75-92	3/4/76	12 mo.
Laboratory investigation of the heterogeneous interaction of Cl and ClO with H_2SO_4	Martin	Aerospace Corporation	75-81	3/22/76	12 mo.
Measurement of HCl, HF, ClO, etc., in the stratosphere by high resolution infrared spectroscopy	Girard	ONERA-France	75-88	3/29/76	12 mo.
Measurement of fluorocarbons and related chlorocarbons in the stratosphere by collection and analysis	Ridley	York U.	76-102	3/31/76	12 mo.[b]
Continuation of 75-13	Murcray	U. of Denver	76-101	4/1/76	12 mo.[b]
Construction of Fourier-transform spectrometer	Buijs	Bomem, Inc.	75-90	4/1/76	12 mo.[b]
Measurement of HCl and HF in the stratosphere by Fourier transform spectroscopy	Buijs	Bomem, Inc.	75-98	4/9/76	5 mo.[a]
Continuation of 75-32	Sze	ERT, Inc.	76-115	6/18/76	11 mo.
Total world ozone level: statistical analysis	Parzen, Pagano	Frontier Science and Technology Research Foundation, Inc.	76-106	7/15/76	12 mo.
The Electron Capture Detector as a Reference Standard in the Analysis of Atmospheric Halocarbons	Lovelock	Private	76-120	8/16/76	12 mo.
Continuation of 75-11	Nicholls	York U.	75-11 II	8/18/76	12 mo.
Continuation of 75-1	Birks	U. of Illinois	76-117A	8/26/76	12 mo.
Studies of Heterogeneous Reactions	Birks	U. of Illinois	76-117B	9/29/76	12 mo.
Studies of Compounds of Sulfur, Oxygen, and Chlorine	Kaufman	Emory U.	76-126	10/7/76	12 mo.

(continued)

Table 5B (continued)

WORK IN PROGRESS

gram	Investigator	Organization	Proposal Number	Contract Date	Contract Period
orological and Multi-Dimensional Modeling nsiderations Relating to Atmospheric Effects Halocarbons	Cunnold, Alyea, Prinn	CAP Associates	76-122	10/8/76	12 mo.
olute Calibration of Fluorocarbon Measurements	Stedman	U. of Michigan	76-132	10/21/76	2 mo.[a]
ochemical and chemical kinetic measurements stratospheric importance with respect to the uorocarbon issue	Timmons	Catholic U.	76-129	10/29/76	12 mo.
l Chlorine Measurements in the Troposphere d Stratosphere	Eggleton	AERE Harwell	76-116	11/2/76	4 mo.
r Magnetic Resonance Study of HO_2 Chemistry	Howard	NOAA-Boulder	76-100	11/6/76	6 mo.
ochemistry of small chlorinated molecules	Wiesenfeld	Cornell	76-128	11/8/76	12 mo.
tospheric measurement of ClO and OH	Murcray	U. of Denver	76-135	12/9/76	4 mo.
atic effects of fluorocarbons	Cunnold, Alyea, Prinn	CAP Associates	76-122S	12/10/76	12 mo.
tions of the HO_2 radical studied by laser gnetic resonance	Thrush	U. of Cambridge	75-58 II	Pending	12 mo.
imeter wave observations of chlorofluoro-thane byproducts in the stratosphere	Solomon	SUNY Stony Brook	76-130	Pending	12 mo.
r stratospheric measurement of non-methane drocarbons	Rasmussen	Private	76-140	Pending	4 mo.
rlaboratory comparisons of fluorocarbon asurements	Rasmussen	Private	76-142	Pending	3 mo.

[a]Contract extended.

[b]Estimate.

Table 6

PUBLICATIONS RESULTING FROM WORK SUPPORTED BY FLUOROCARBON MANUFACTURERS

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1. Four-Center Reactions Involving Dichlorine Monoxide, J.W.B., B. Shoemaker, T. J. Lock, and D. M. Hinton, draft ms.

2. Studies of Reactions of Importance in the Stratosphere. I. Reaction of Nitric Oxide With Ozone, J.W.B., B. Shoemaker, T. J. Lock, and D. M. Hinton, draft ms.

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1. Halocarbon Decomposition by Natural Ionization, M.J.C., Geophys. Res. Lett., 3 (11), 661-4 (1976).

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1. The Impact of Stratospheric Variability on Measurement Programs for Minor Constituents, R.G.P., F.N.A., and D.M.C., Bull. Am. Meteorol. Soc., 57 (6), 686-94 (1976).

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2. Measurement of the Reaction Rate of CF_3Cl with Atmosphere-Like Ions, R. G. Hirsch, Atmos. Environ., 10 (9), 703-5 (1976).

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4. Photochemical Oxidation of Halocarbons in the Troposphere, R. A. Cox, R. F. Derwent, A. E. J. Eggleton, and J.E.L., Atmos. Environ., 10 (4), 305-8 (1976).

5. Halocarbon Behavior from a Long Time Series, D. H. Pack, J.E.L., C. Cotton, and C. Curthoys, draft ms.

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1. Simultaneous Stratospheric Measurements of Fluorocarbons and Odd Nitrogen Compounds, W. J. Williams, J. J. Kosters, A. Goldman, and D.G.M., draft ms.

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